

5. OCCUPATIONAL EXPOSURE AND HAZARD ANALYSIS¹

5.1 INTRODUCTION

This chapter presents an analysis of potential occupational exposures to alternative propellants and solvents used in aerosol spray applications. Currently, several Class I compounds are used in a wide variety of aerosol applications, with CFC-12 and CFC-114 being used as propellants and CFC-11, CFC-113, and methyl chloroform being used as aerosol solvents. Potential substitutes for these materials include HCFCs, HFCs, chlorinated hydrocarbons, aliphatic hydrocarbons, and compressed gases. The composition of aerosol products is varied; Exhibit 5-1 shows the percent content of propellant and solvent for several types of aerosol products.

EXHIBIT 5-1
FORMULATIONS OF SOME COMMON AEROSOL PRODUCTS

Product	Percent Content	
	Propellant	Solvent
Polyurethane coating	25	60
Adhesives	15	60
Polishes	4 to 15	Up to 30
Spot removers	45 to 50	40 to 45
Spray enamel	30	60
Dusters	100	--

Source: *Clinical Toxicology of Commercial Products*. 5th Edition. Gosselin, R.E., Smith, R.P., and Hodge, H.C. (eds.). Baltimore: William & Wilkins.

Potential occupational exposures associated with the use of aerosol propellant and solvent substitutes were evaluated for two industrial operations: aerosol can filling and aerosol use. Air monitoring data describing worker exposures during aerosol can filling operations were available from the docket for the Occupational Safety and Health Administration's (OSHA's) proposed rule for methylene chloride and a published NIOSH report; this evaluation of potential occupational exposures to propellant and solvent substitutes used in this operation is based solely on these data.

Few air monitoring data were available that described worker exposures to propellants and solvents during the industrial use of aerosol products. Occupational exposures associated with the use of aerosol products were evaluated using a mass-balance model that estimates the magnitude of exposure given a specific contaminant release rate and rate of fresh air exchange. The results obtained from the model are compared to the occupational exposure limits established for each substance (see Chapter 3).

¹ This section was prepared by an industrial hygienist certified by the American Board of Industrial Hygiene.

The following section describes the model used in this analysis; this is followed by a discussion of the results obtained.

5.2 DESCRIPTION OF THE MODEL

The modeling approach used in this analysis requires the use of several assumptions to simulate the initial increase and subsequent decrease in airborne contaminant concentrations resulting from the release of the contaminant. Specifically, the assumptions needed to perform this kind of analysis include:

- The size (volume) of the space in which the contaminant is released;
- The rate at which fresh air infiltrates the space; and
- The amount and rate of contaminant release (i.e., the rate at which the aerosol product is used).

The model that is used is derived from a differential material balance that, when integrated, provides a basis for relating air concentration of contaminant to the generation and removal rates of a contaminant. This model has been widely used for many years to estimate probable exposures of workers to hazardous airborne materials, and has been described in detail by the National Institute for Occupational Safety and Health (NIOSH 1973). Starting with a fundamental material balance equation, assuming no contaminant is in the supply air:

Rate of Accumulation = Rate of Generation - Rate of Removal

$$VdC = Gdt - Q'Cdt \quad (\text{Equation 3-1})_1$$

Where:

C = Concentration of gas or vapor at time t

G = Rate of generation of the contaminant (CFM)

Q' = Effective rate of ventilation that is corrected for incomplete mixing (CFM) (a mixing factor of 0.5 is used which, when multiplied by the actual ventilation rate, yields Q')

V = Volume of room or enclosure (ft³)

Rearranging, integrating, and further simplifying the material balance equation yields the final equation used to estimate contaminant concentration during the release of the contaminant:

$$\int_{C_1}^{C_2} \frac{dC}{G - Q'C} = \frac{1}{V} \int_{t_1}^{t_2} dt \quad (\text{Equation 3-2})_2$$

$$\ln \left(\frac{G - Q'C_2}{G - Q'C_1} \right) = -\frac{Q'}{V} (t_2 - t_1) \quad (\text{Equation 3-3})_3$$

$$\frac{G - Q'C_2}{G - Q'C_1} = e^{-\frac{Q'}{V} (t_2 - t_1)} \quad (\text{Equation 3-4})_4$$

Assuming that there is no initial concentration at time = 0 (i.e., $C_1 = 0$), then

$$C_2(ppm) = \frac{G \left[1 - e^{\left[-\frac{Q'}{V} (t_2 - t_1) \right]} \right]}{Q'} \times 10^6 \quad (\text{Equation 3-5})$$

When the release of contaminant stops, the air concentration declines as the contaminant is diluted by fresh air. That is:

Rate of Accumulation = Rate of Removal

$$VdC = -Q'Cdt \quad (\text{Equation 3-6})$$

Rearranging, integrating, and further simplifying this material balance equation results in the equation used to estimate contaminant concentration after a given period of dilution:

$$\int_{C_1}^{C_2} \frac{dC}{C} = -\frac{Q'}{V} \int_{t_1}^{t_2} dt \quad (\text{Equation 3-7})$$

$$\ln \left(\frac{C_2}{C_1} \right) = -\frac{Q'}{V} (t_2 - t_1) \quad (\text{Equation 3-8})$$

$$\frac{C_2}{C_1} = e^{-\frac{Q'}{V} (t_2 - t_1)} \quad (\text{Equation 3-9})$$

$$C_2 = C_1 e^{-\frac{Q'}{V} (t_2 - t_1)} \quad (\text{Equation 3-10})$$

0

As a worst-case assumption, it was assumed that an employee used 1,000 grams of aerosol product over an 8-hour shift. Exhibit 5-1 above indicates that the maximum solvent content of any aerosol product is 60 percent, and the maximum propellant content of any aerosol product is 50 percent (excluding dusters, which are comprised entirely of propellant). Therefore, to evaluate potential worker exposures to propellants and solvents, it was assumed that the release rates for propellants and solvents are 500 and 600 grams, respectively, over an 8-hour shift.

Workers were assumed to perform their job function at a fixed workstation throughout the shift and were assumed not move to other areas that are free from airborne contamination by aerosol products. This is a worst-case assumption in that exposures will be lower than estimated to the extent that workers spend part of their shifts performing tasks that do not involve the use of aerosol products.

Because the worker will be in close proximity to the point of contaminant emission during the use of an aerosol product, localized airborne concentrations of propellants and solvents were calculated from the model assuming that the worker is approximately 18 inches from the emission point. Thus, the

volume of space occupied by the contaminant is represented by a space having dimensions of 3 x 3 x 3 feet and a volume of 27 ft³. The air exchange rate used in the model is based on the velocity of air moving through this space; as a worst-case assumption, it was assumed that air moves through the space occupied by the contaminant at a rate of 50 feet per minute (fpm), which is often taken as the minimum air velocity that results from local air currents in the absence of any mechanical ventilation (ACGIH 1982). To evaluate the effect of supplying local exhaust ventilation on reducing exposures to aerosol constituents, the air velocity was increased to 150 fpm in the model runs, which is the ACGIH-recommended face velocity for a small benchtop spray booth (ACGIH 1982).

To evaluate short-term (i.e., 30-minute) exposures to aerosol propellants or solvents, it was assumed that a worker discharged a 1-pound can of product over 15 minutes in the absence of any mechanical ventilation.

5.3 RESULTS

5.3.1 Aerosol Can Filling

Two published sources contain information on occupational exposures to aerosol constituents during aerosol can filling operations. One report is a study published by the National Institute for Occupational Safety and Health (NIOSH 1978) that contains air monitoring data obtained from one facility that manufactures an aerosol product containing solvent mixtures and CFC-12 propellant. In this operation, aerosol products are formulated in batches and pumped to a can filling station. Cans are partially filled with the solvent mixture from an automatic can filling machine; spray valve caps are then machine-fed into each can, after which CFC-12 is automatically injected to pressurize the cans.

Personal air samples representing the major portion of the work shift were collected on seven employees working at this facility. Exposures to CFC-12 ranged from 6.2 to 53.9 ppm and represented the highest exposures recorded at the facility during this operation. Exposures to solvent constituents (CFC-11, methylene chloride, trichloroethylene, perchloroethylene, and 1,1,1-trichloroethane) were generally below 10 ppm and did not exceed 15.5 ppm. At the time of the survey, the building in which the operation is conducted was open and appeared to have good natural ventilation that was assisted by the use of pedestal and wall-mounted fans. According to the investigators, the intermittency of the aerosol can filling operation combined with the general building ventilation provided for the rapid dissipation of contaminant emissions.

OSHA evaluated data describing worker exposures to methylene chloride during aerosol paint can filling operations as part of their analysis for a proposed occupational standard for methylene chloride (56 *FR* 57036). In this operation, liquid methylene chloride is fed into cans by a metered injection pump, after which the propellant is injected and valve stem installed in an explosion-proof room. Data obtained by OSHA during a site visit indicated that employee exposures to methylene chloride ranged from 11 to 67 ppm as an 8-hour time-weighted average (TWA) concentration. OSHA identified three engineering approaches that could be used to reduce employee exposures below the 25 ppm PEL being proposed by the Agency:

- Use of a chilling system to lower the temperature of liquid methylene chloride from ambient levels to 20° F, which was estimated to reduce emissions and exposures by 75 percent;
- Increasing the capacity of slot hood ventilation provided at the can filling station; and
- Enclosing and ventilating the conveyor on which the cans are filled and charged.

Because the PEL being proposed by OSHA for methylene chloride is among the most stringent of any of the PELs established for substitute aerosol solvents, EPA believes that these engineering approaches, none of which is unique to the operations conducted at the facility visited by OSHA, would prove to be equally successful for maintaining occupational exposures below the PEL for any aerosol solvent substitute. For substitute propellants, the ventilation approaches described above would be the most effective means of controlling worker exposure.

5.3.2 Aerosol Product Use

The mass balance model and approach described above were used to estimate occupational exposures from the industrial use of aerosol products. Exhibit 5-2 presents the results of this analysis, along with the occupational exposure limits. A comparison of the estimated exposure levels with the Workplace Guidance Levels (WGLs) and Emergency Guidance Levels (EGLs) indicates that worker exposures to propellant and solvent substitutes are not likely to exceed occupational exposure limits for these materials under the assumed conditions of use, even in the absence of suitable local exhaust ventilation. The model results also suggest that the use of a small ventilated spray booth meeting the design criteria recommended by the ACGIH should prove effective in maintaining worker exposures below established limits for all of the propellant and solvent substitutes identified.

In the absence of local exhaust ventilation, estimated short-term exposures exceed established occupational limits in only a few instances even under the conditions of high-volume aerosol use assumed for the model; the use of spray booths having a minimum of 150 fpm face velocity would be expected to reduce these estimates by two-thirds.

Available air monitoring data confirm the basic finding from the model that employee exposures do not generally exceed established exposure limits during the use of aerosol products. Data contained in a submittal to EPA indicates that workers using an aerosol agent in an in-line electronics degreaser were not exposed above 9.4 ppm of HCFC-141b. This same source reported that employees using a spray formulation containing CFC-113 were not exposed above 27 ppm (for a 5-hour sample), well below OSHA's 1,000 ppm PEL for this substance.

Whitehead et al. (1984) measured the exposure of employees to a variety of solvents during spray painting and spray gluing operations at three industrial facilities. Although material was applied using compressed air or airless spraying equipment, rather than from pressurized aerosol cans, the study is useful for illustrating the effectiveness of local exhaust ventilation in reducing employee exposures to solvent emissions generated during spraying operations. All employees sampled performed spraying operations in either walk-in or benchtop spray booths having face velocities ranging from 50 to 250 fpm. A total of 89 full-shift exposure measurements were made. Of these, only one sample exceeded the ACGIH Threshold Limit Value (TLV) for a solvent (in this case, methylene chloride), and only two others exceeded 50 percent of the TLV for the solvent analyzed.

EXHIBIT 5-2
OCCUPATIONAL EXPOSURE LIMITS AND ESTIMATED 8-HOUR TWA AND
30-MINUTE EXPOSURES TO AEROSOL PROPELLANT AND SOLVENT SUBSTITUTES

	OELs ^a		Estimated Exposure, 8-HR TWA		
	WGL (ppm)	EGL (ppm)	No LEV ^b (ppm)	LEV ^b (ppm)	30-MIN TWA (ppm)
Propellants					
<u>Hydrocarbons</u>					
n-Butane	800		68.9	23.0	500
Isobutane		750	68.9	23.0	500
Pentane	600	750	55.5	18.5	403
<u>HCFCs</u>					
HCFC-22	1,000	5,000	46.3	15.4	337
HCFC-141b	500	1,000	41.1	13.7	298
HCFC-142b	1,000	5,000	39.7	13.2	288
<u>HFCs</u>					
HFC-134a	1,000	3,000	39.3	13.1	285
HFC-152a	1,000	5,000	60.7	20.2	441
HFC-125	1,000	3,000	33.3	11.1	250
<u>Compressed Gases</u>					
Carbon Dioxide	10,000	30,000	91.0	30.3	661
Dimethyl Ether		500	86.9	29.0	632
Solvents/Diluents					
<u>Petroleum</u>					
<u>Based Hydrocarbons</u>					
3-Methylhexane	400 ^c	500 ^c	48.0	16.0	290
3-Methylpentane	500 ^d	1,000 ^d	55.8	18.6	338
2,3-Dimethylpentane	400 ^c	500 ^c	51.0	17.0	309
n-Heptane	400	500	48.0	16.0	290
n-Hexane	50		55.8	18.6	338
n-Octane	300	375	42.1	14.0	255
5-Methylnonane	400 ^c	500 ^c	33.8	11.3	204
n-Decane	400 ^c	500 ^c	33.8	11.3	204
Toluene	100	150	52.2	17.4	316
Xylene	100	150	45.3	15.1	274
<u>Oxidized Hydrocarbons</u>					
Methanol	200	250	150.0	50.0	908
Ethanol	1,000		104.3	34.8	632
Isopropanol	400	500	80.0	26.7	484
Acetone	750	1,000	82.8	27.6	501
Ethyl Acetate	400		54.6	18.2	230

EXHIBIT 5-2 (continued)
OCCUPATIONAL EXPOSURE LIMITS AND ESTIMATED 8-HOUR TWA AND
30-MINUTE EXPOSURES TO AEROSOL PROPELLANT AND SOLVENT SUBSTITUTES

	OELs ^a		Estimated Exposure, 8-HR TWA		
	WGL (ppm)	EGL (ppm)	No LEV ^b (ppm)	LEV ^b (ppm)	30-MIN TWA (ppm)
<u>Terpenes</u>					
d-Limonene	25		35.8	11.8	214
<u>Chlorinated Solvents</u>					
Methylene Chloride	25		56.6	18.9	343
Perchloroethylene	25	200	29.0	9.7	175
Trichloroethylene	50		36.6	12.2	222

^a See Chapter 3

^b Local Exhaust Ventilation

^c Limits for petroleum distillates

^d Limits for hexane isomers

5.4 FLAMMABILITY CONSIDERATIONS

A number of the substitutes that have been identified for aerosol propellants and solvents are flammable; Exhibit 5-3 lists the flammable properties for these materials. For many industrial uses of aerosols, flammable materials can be used safely so long as appropriate precautions are taken to prevent the localized buildup of gas or vapor to levels exceeding the lower explosive limit (LEL), to isolate potential sources of ignition from the aerosol operation, and to provide for appropriate storage and other fire protection measures. In general, the use of aerosol products in well-ventilated areas should not result in gas or vapor concentrations exceeding the LEL for the flammable substances used, except along the relatively confined path along which the spray travels; thus, aerosol products containing flammable materials can be safely used by keeping possible sources of ignition away from the vicinity of the spraying operation (i.e., by prohibiting smoking in the work area and using aerosol products away from open flames or electrical systems).

A limited number of work operations may require the use of aerosol products in the immediate vicinity of potential sources of ignition. Examples include the use of aerosol mold release agents, which may be applied to hot surfaces, or the use of electronic cleaning agents that are applied to electrically-charged components. In these instances, the use of aerosol products containing flammable materials may present a safety hazard from the ignition of the propellant or solvent at the point of application, followed by the possibility of a flash back towards the can. The use of liquids having flash points at or below 100°F would be prohibited by OSHA standards in these applications; 29 *CFR* 1910.106(e)(c) specifies that Class I liquids (those with flash points below 100°F) may be used "only where there are no open flames or other sources of ignition within the possible path of vapor travel".

EXHIBIT 5-3
FLAMMABLE PROPERTIES OF AEROSOL SUBSTITUTES

	Lower Explosive Limit (Percent in Air)	Auto Ignition Temperature (°F)	Flash Point (°F)
GASES			
Butane	1.6	550	-76
Isobutane	1.9	864	
Pentane	1.5	588	-40
Dimethyl Ether	3.4	662	
HFC-152a	3.9		
HCFC-142b	6.9	>600	
HFC-143a	7.1		
LIQUIDS			
n-Hexane	1.1	437	-7
Acetone	2.5	869	-4
2,3-Dimethylpentane	1.1	635	<20
3-Methylpentane	1.2	532	<20
Ethyl Acetate	2.0	800	24
n-Heptane	1.1	399	25
3-Methylhexane		536	25
Toluene	1.2	896	40
Methanol	6.0	867	52
Isopropanol	2.0	750	53
Ethanol	3.3	685	55
n-Octane	1.0	403	56
Xylene	1.1	867	81
n-Decane	0.8	410	115
Methylene Chloride	14.0	1,033	None
HCFC-141b	7.4	550	None
Trichloroethylene	8.0	788	None
d-Limonene	0.7	458	113

REFERENCES

- ACGIH. 1982. *Industrial Ventilation: A Manual of Recommended Practice, 17th Edition*. Chapter 4.
- NIOSH (Mutchler, J.E.). 1973. "Principles of Ventilation." *The Industrial Environment--It's Evaluation and Control*. Center for Disease Control, U.S. Department of Health and Human Services. ch. 39.
- NIOSH. 1978. *Fluorocarbons--An Industrial Hygiene Survey of Worker Exposure in Four Facilities*. Report No. NIOSH 79-101.
- Whitehead, L.W., G.L. Ball, L.J. Fine, G.D. Langolf. 1984. "Solvent Vapor Exposures in Booth Spray Painting and Spray Glueing, and Associated Operations." *American Industrial Hygiene Association Journal*. Vol. 45, No. 11, pp. 767-772. November 1984.